

APPLICAZIONI INDUSTRIALI DELLA CATALISI OMOGENEA E FOTOCATALISI

(6 CFU)

Struttura del corso

CHIMICA ORGANOMETALLICA

Prof.ssa Elisabetta Iengo (2 CFU)

CATALISI OMOGENEA e FOTOCATALISI

Prof.ssa Barbara Milani (4 CFU)

Trattazione dei principi base della catalisi omogenea

Studio di alcuni processi industriali basati sulla catalisi omogenea

Attivazione del biossido di carbonio

Introduzione alla fotocatalisi omogenea

Esame finale: prova orale unica sui due moduli.

Testi consigliati:

❖ Homogeneous Catalysis: understanding the art

Autore: Piet W.N.M. van Leeuwen

Kluwer Academy Publisher

Springer: www.springer.com/chemistry

❖ Inorganic Chemistry Third Edition

Catherine E. Housecroft and Alan G. Sharpe

Pearson Prentice Hall

❖ Inorganic Chemistry Fourth Edition

Shriver & Atkins

Oxford University Press

❖ Fundamentals of Organometallic Catalysis

Dirk Steinborn

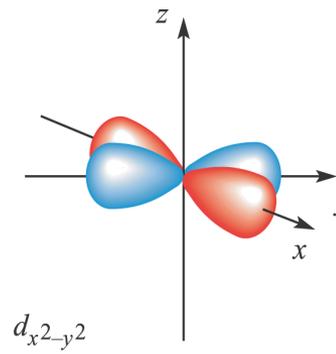
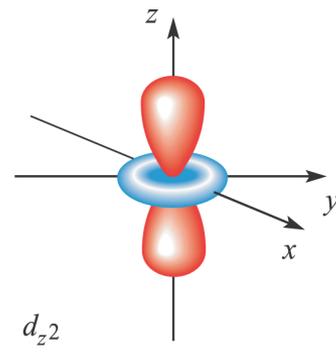
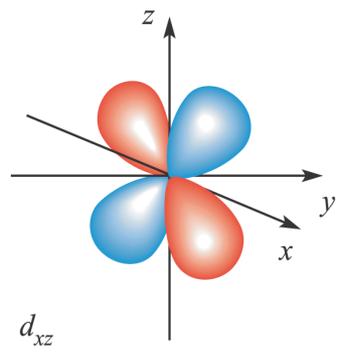
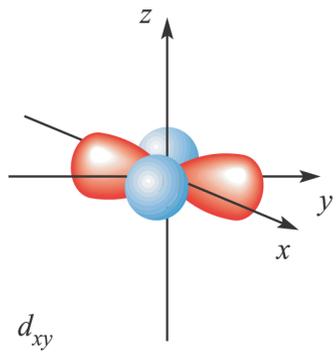
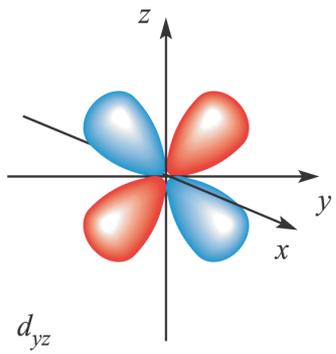
Wiley-VCH (2012)

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❖ Organometallics and Catalysis: an Introduction

Manfred Bochmann

Oxford University Press 2015



Complessi di coordinazione (Werner's type complexes)

- hanno tipicamente leganti semplici, σ -donatori e π -donatori
- normalmente sono carichi
- hanno numero variabile (i.e. non fisso) di elettroni d
- sono (di solito) solubili in acqua

Composti organometallici (almeno un legame M–C)

- sono spesso neutri
- hanno numero fisso di elettroni d (configurazioni elettroniche stabili a 16 o 18 elettroni)
- sono solubili in solventi organici (e.g. THF)
- spesso hanno proprietà che sono molto più simili a quelle dei composti organici che dei sali inorganici (e.g. bassi punti di fusione; alcuni sono liquidi a r.t.)

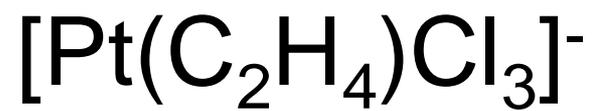
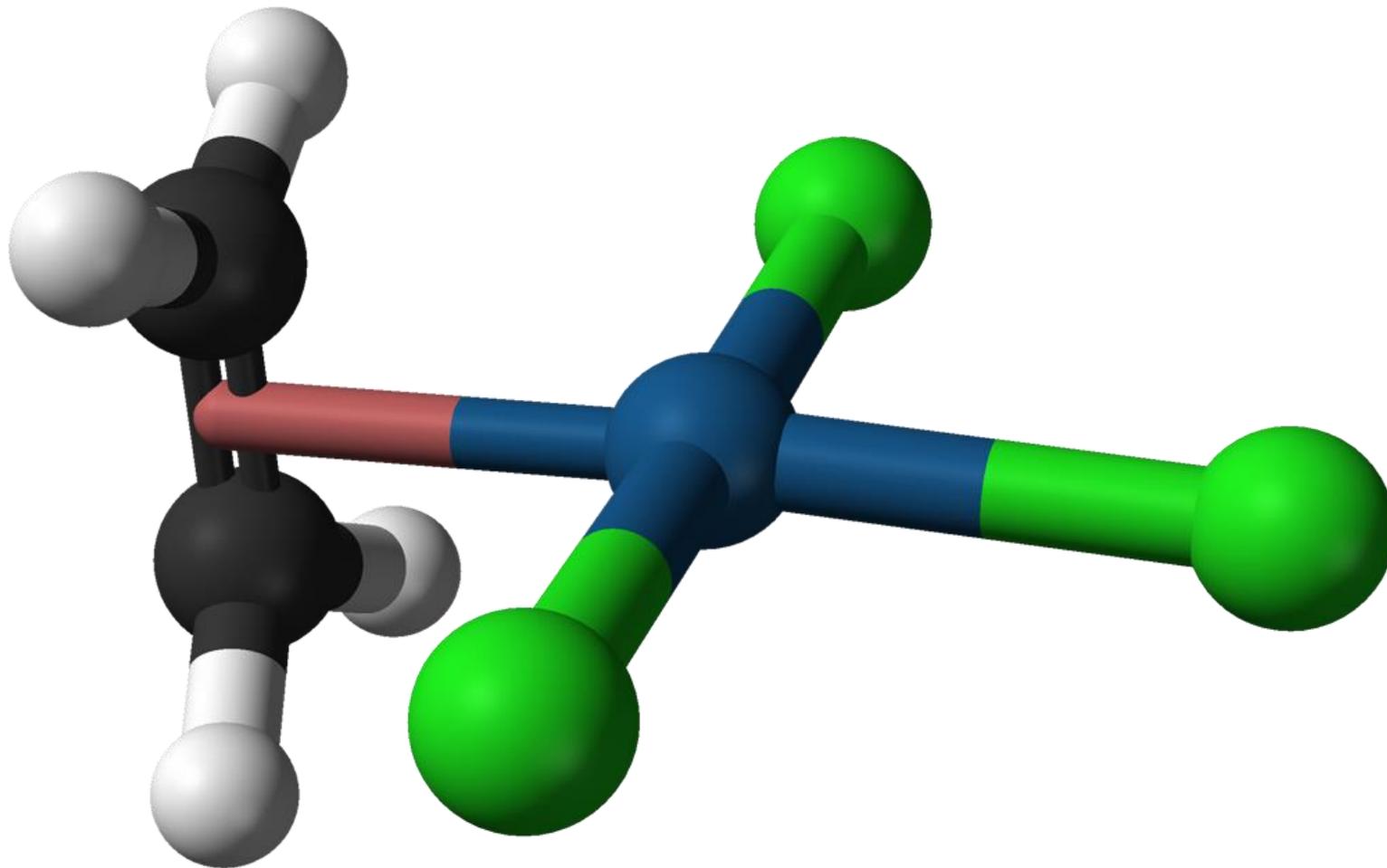


W C Zeise, Danish
pharmacist, **1789- 1847**

'The breakthrough, the isolation of a pure, crystalline compound came when Zeise added potassium chloride to a concentrated PtCl_4 /ethyl alcohol reaction solution and evaporated the resulting solution. Beautiful lemon yellow crystals, often one half inch or more in length were isolated. On longer exposure to air and light, they gradually became covered with a black crust. They contained water of hydration, which was lost when they were kept over concentrated sulfuric acid in vacuo or when heated to around 100°C . Chemists in those days often reported how the compounds that they had prepared tasted. Zeise described the taste of this potassium salt as metallic, astringent and long lasting.'

Dietmar Seyferth, Organometallics, 2001, 20, 2

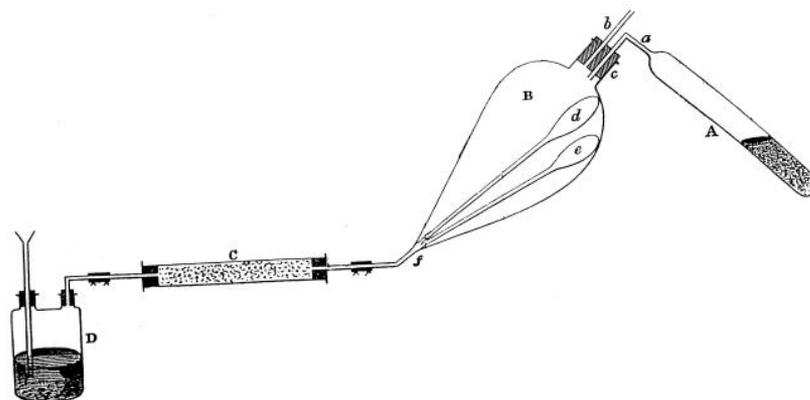
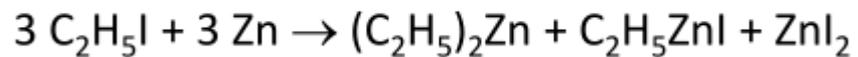




Sale di Zeise, 1827



Edward Frankland
1825-1899



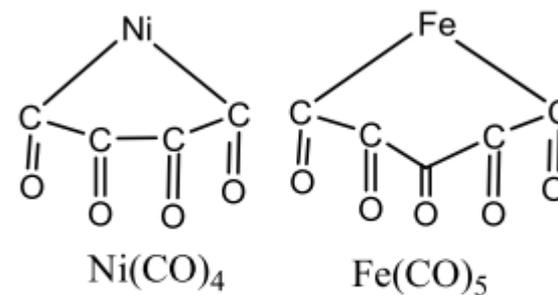
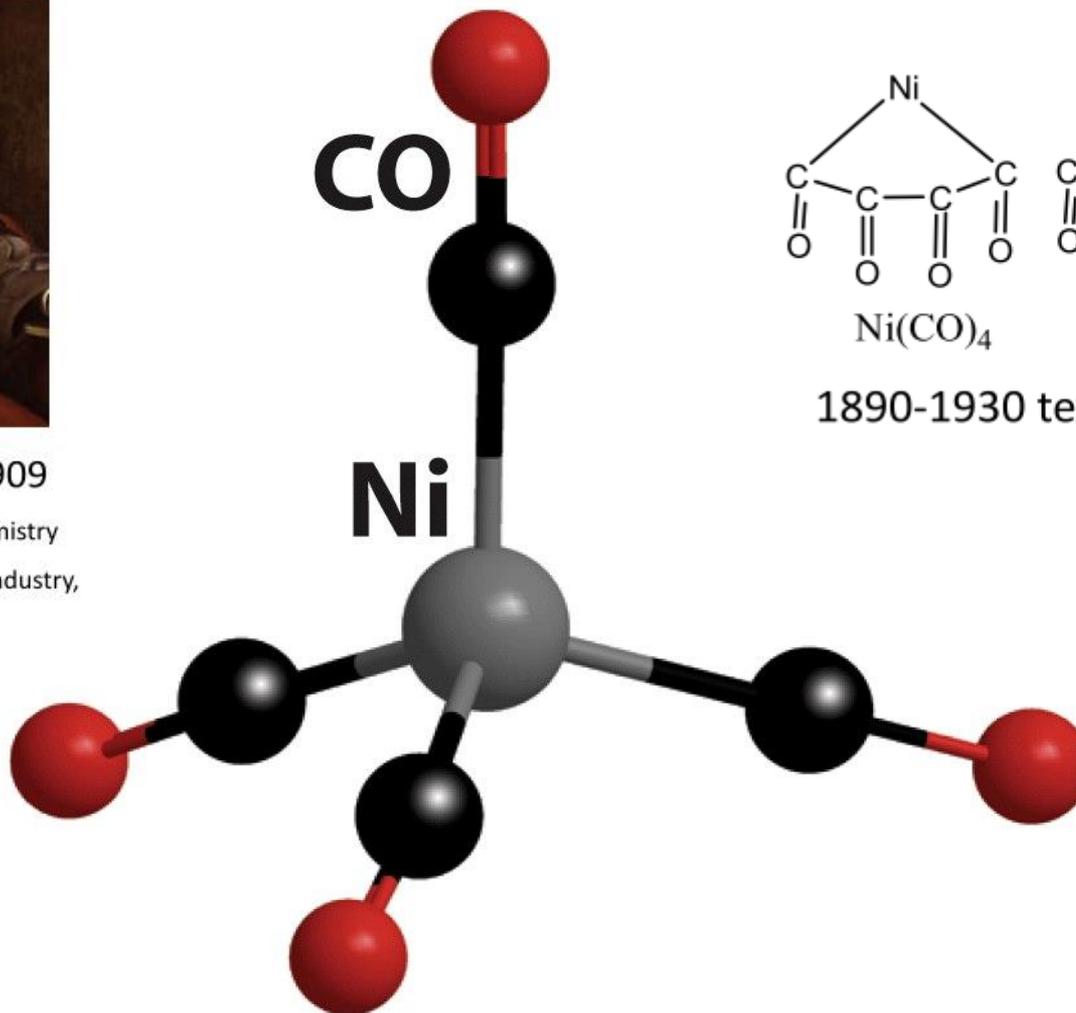
As the early 1850s English chemist Edward Frankland described flasks exploding, throwing bright green flames across his lab, as he heroically distilled dialkylzinc compounds under an atmosphere of **hydrogen**.



Ludwig Mond 1839-1909

Father of Metal Carbonyl Chemistry

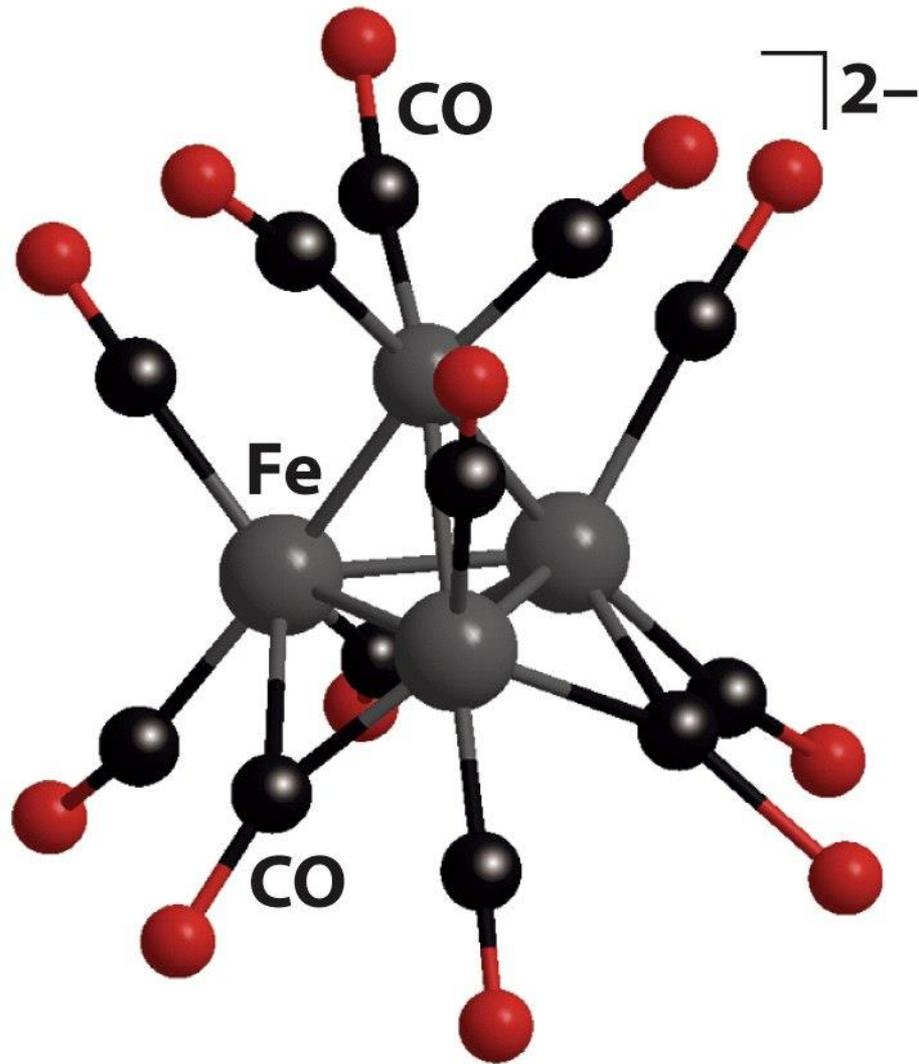
Founder of Imperial Chemical Industry,
England



1890-1930 textbooks



Mond, Langer, Quinke, 1890



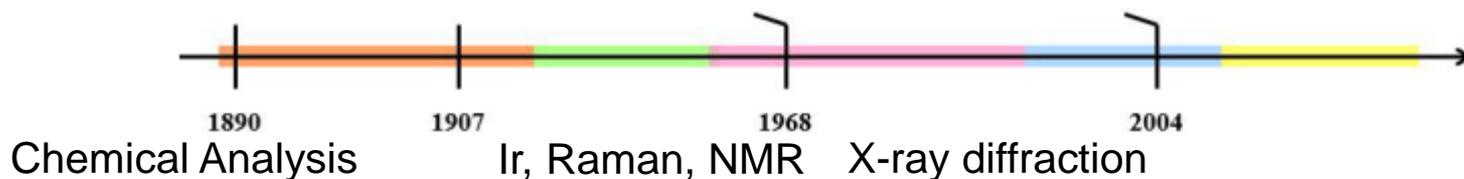
Hieber, 1930-....

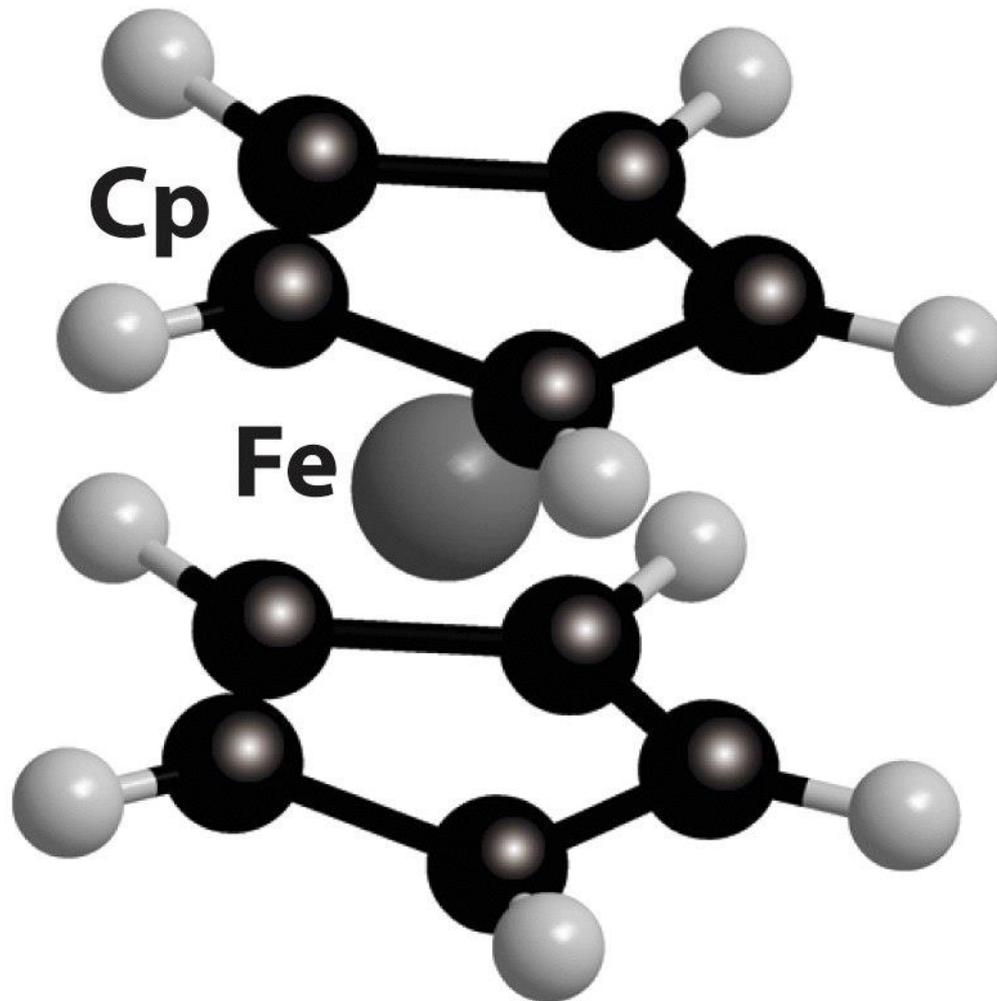


Walter Otto Hieber (1895-1876)
Technische Hochschule München

1868	$\text{Pt}(\text{CO})_2\text{Cl}_2$	M.P. Schützenberger
1890	$\text{Ni}(\text{CO})_4$	L. Mond et al.
1891	$\text{Fe}(\text{CO})_5$	L. Mond, F. Quinke, M. Berthelot
1905	$\text{Fe}_2(\text{CO})_9$	J. Dewar, H.O. Jones
1907	$[\text{Fe}_3(\text{CO})_{12}]^*$	
1910	$\text{Co}_2(\text{CO})_8$	L. Mond et al.
	$\text{Co}_4(\text{CO})_{12}$	
1910	$\text{Mo}(\text{CO})_6$	
1927/28	$\text{Cr}(\text{CO})_6$	A. Job et al.
	$\text{W}(\text{CO})_6$	

“... it was only in the autumn of 1927 at the Institute of Chemistry of the University of Heidelberg that I took up research experiments with iron pentacarbonyl, which was kindly provided by Dr. A. Mittasch of BASF ... On the basis of his own experience with nickel carbonyl he warned me emphatically of the danger inherent in the use of these highly toxic substance, coupling his warning with the comment that in this field one could only expect a great deal of trouble and results of little scientific value!”





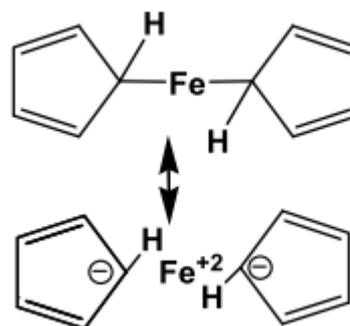
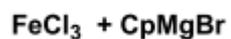
Ferrocene, 1951 (IR, X-ray, NMR)



Pauson



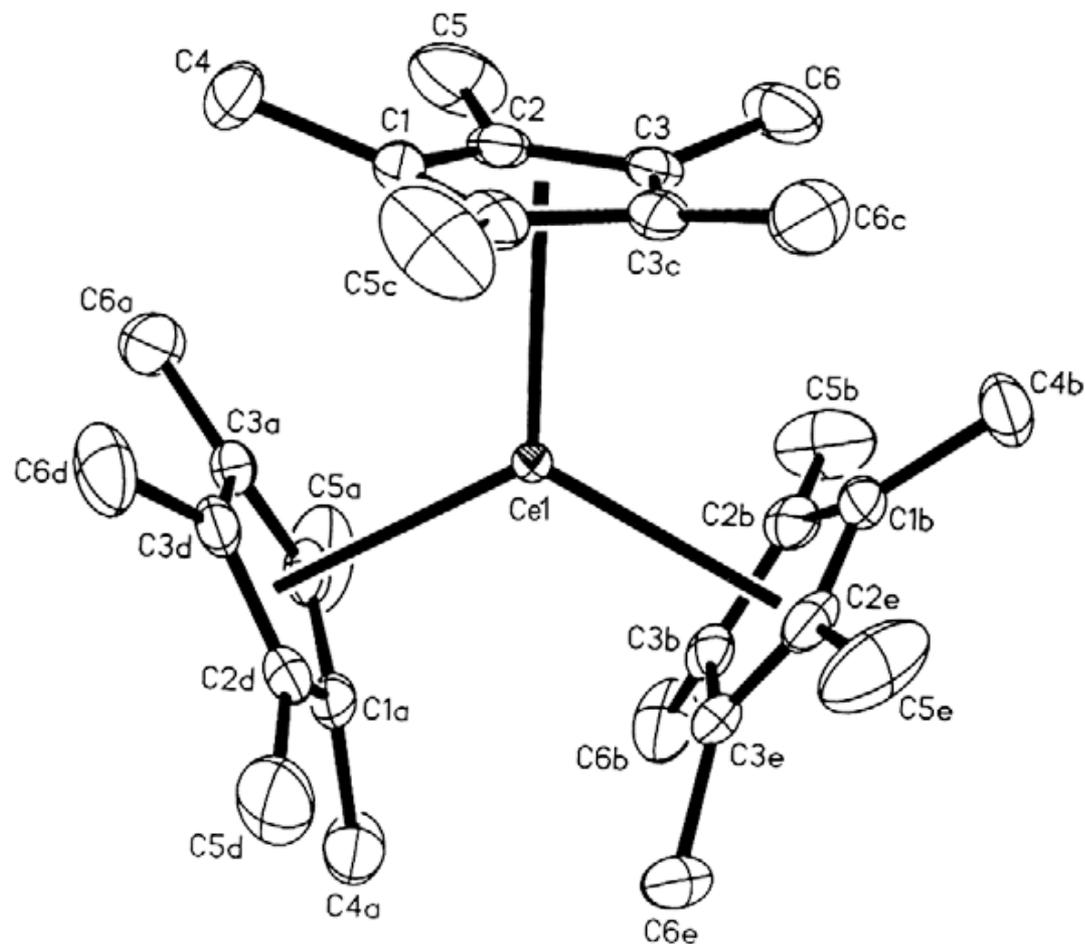
Kealy



A New Type of Organo-Iron Compound

letters to nature

Nature **168**, 1039 - 1040 (15 December 1951); doi:10.1038/1681039b0



1970 - ... Ln-Cp* compounds
 $\text{Cp}^* = \text{C}_5\text{Me}_5^-$

1973

Premio Nobel

per la Chimica Organometallica
degli elementi del blocco d

Ernst-Otto Fisher (Monaco di Baviera)

e

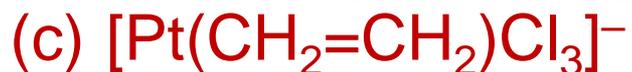
Geoffrey Wilkinson (Londra)

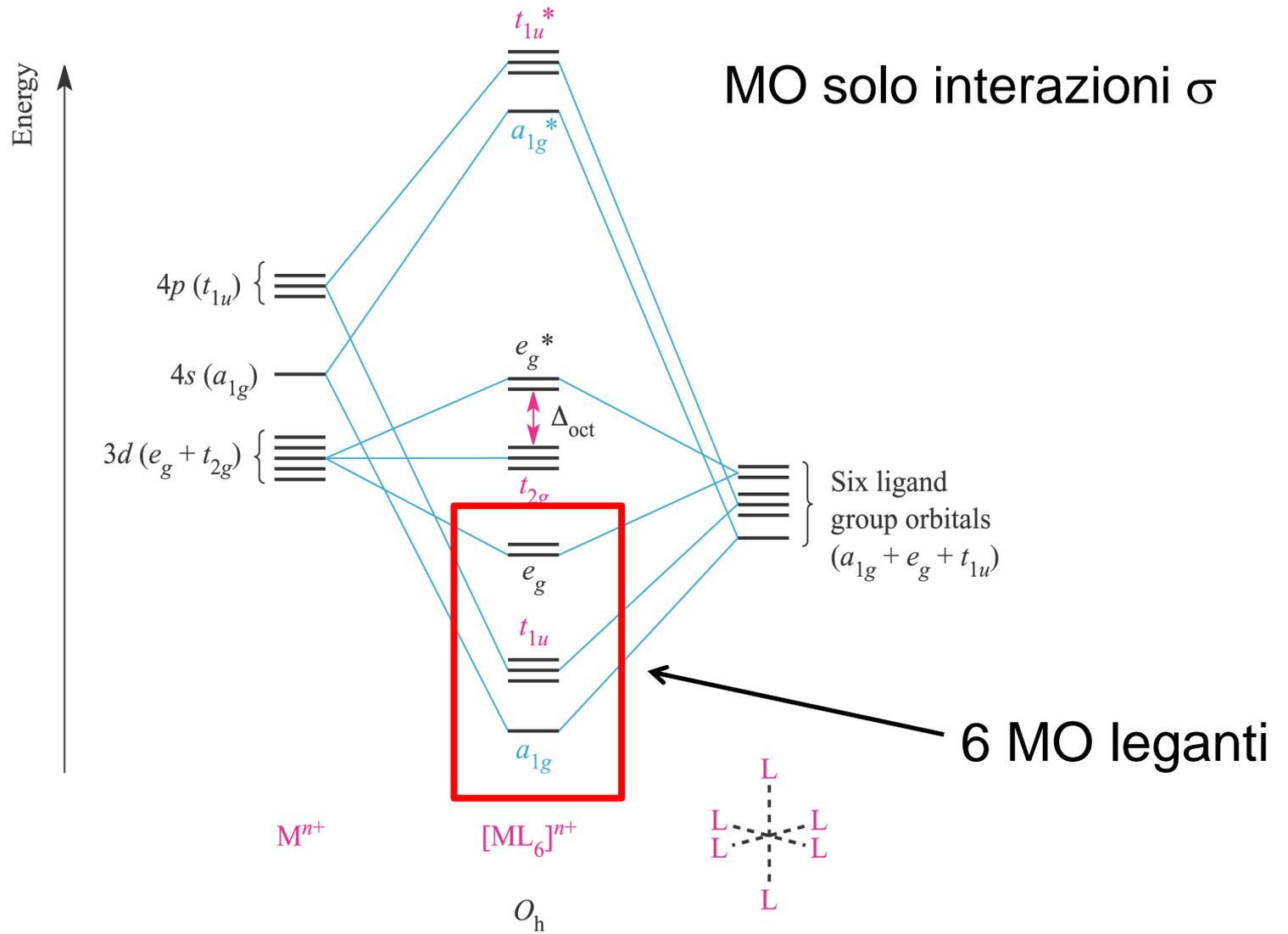
Conta degli elettroni: metodo della donazione di coppie elettroniche

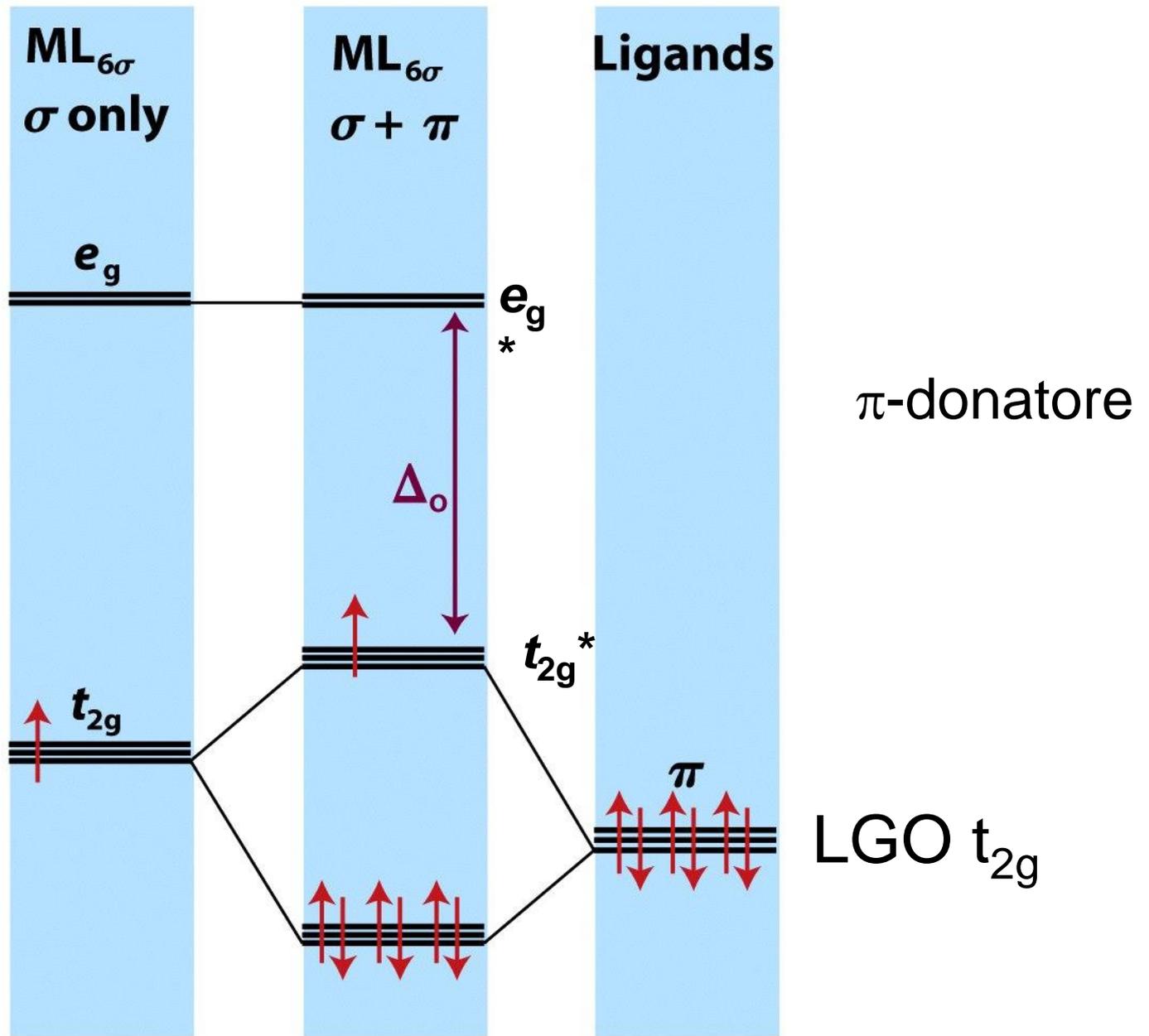
Ligand	Formula	Electrons donated
Carbonyl	CO	2
Phosphine	PR ₃	2
Hydride	H ⁻	2
Dihydrogen	H ₂	2
η^1 -Alkyl, -alkenyl, -alkynyl, and -aryl groups	R ⁻	2
η^2 -Alkene	CH ₂ =CH ₂	2
η^2 -Alkyne	RCCR	2
Dinitrogen	N ₂	2
Butadiene	CH ₂ =CH—CH=CH ₂	4
Benzene	C ₆ H ₆	6
η^3 -Allyl	CH ₂ CHCH ₂ ⁻	4
η^5 -Cyclopentadienyl	C ₅ H ₅ ⁻	6

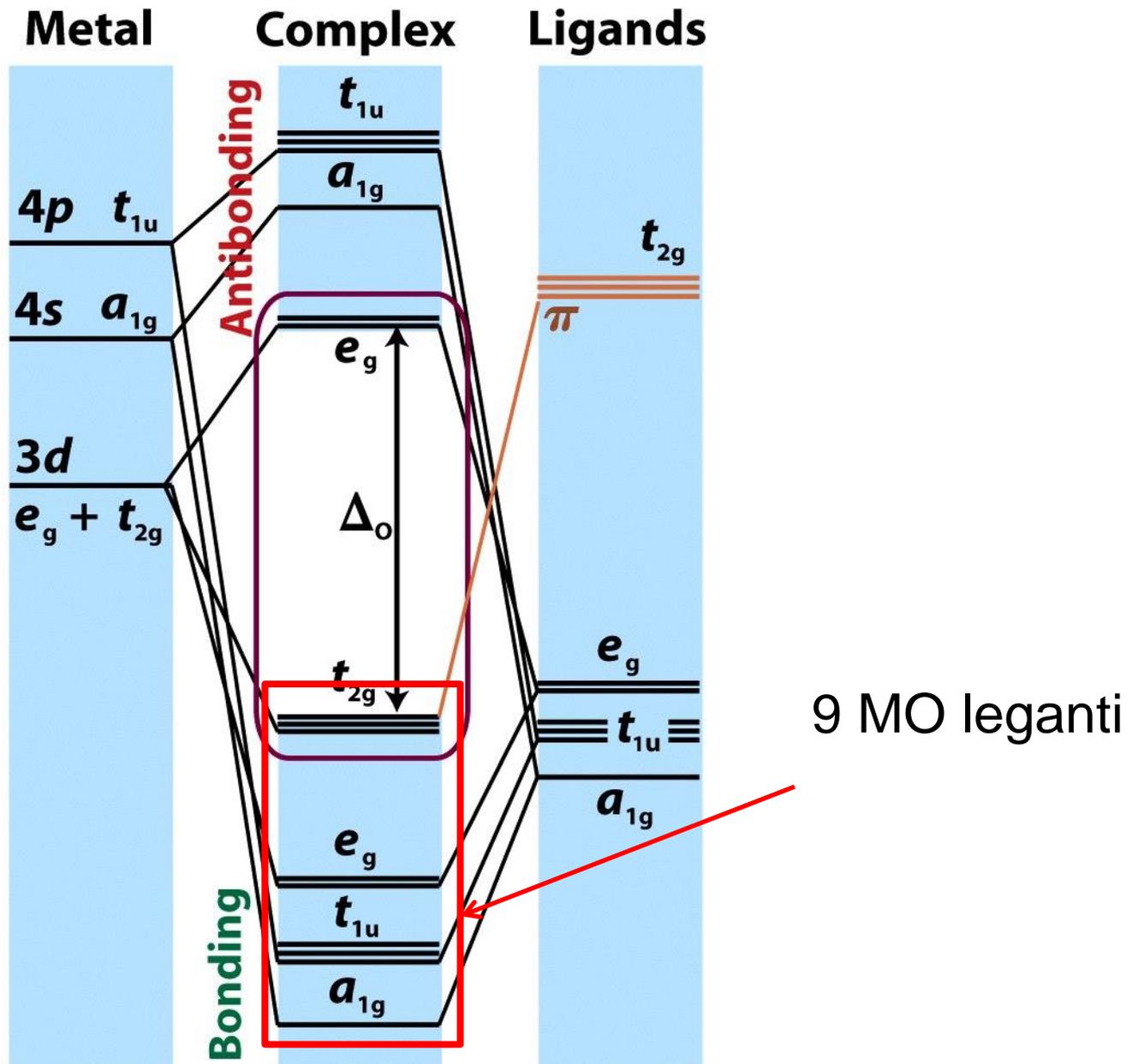
* We use this method throughout this book.

- Il *numero di ossidazione* dell'atomo metallico è dato dalla carica totale del complesso meno le eventuali cariche dei leganti.
- Il *numero di elettroni* forniti dal metallo corrisponde a quello del suo Gruppo meno il suo numero di ossidazione.
- Il *numero totale di elettroni* è la somma del numero di elettroni sull'atomo metallico e del numero di elettroni forniti dai leganti.

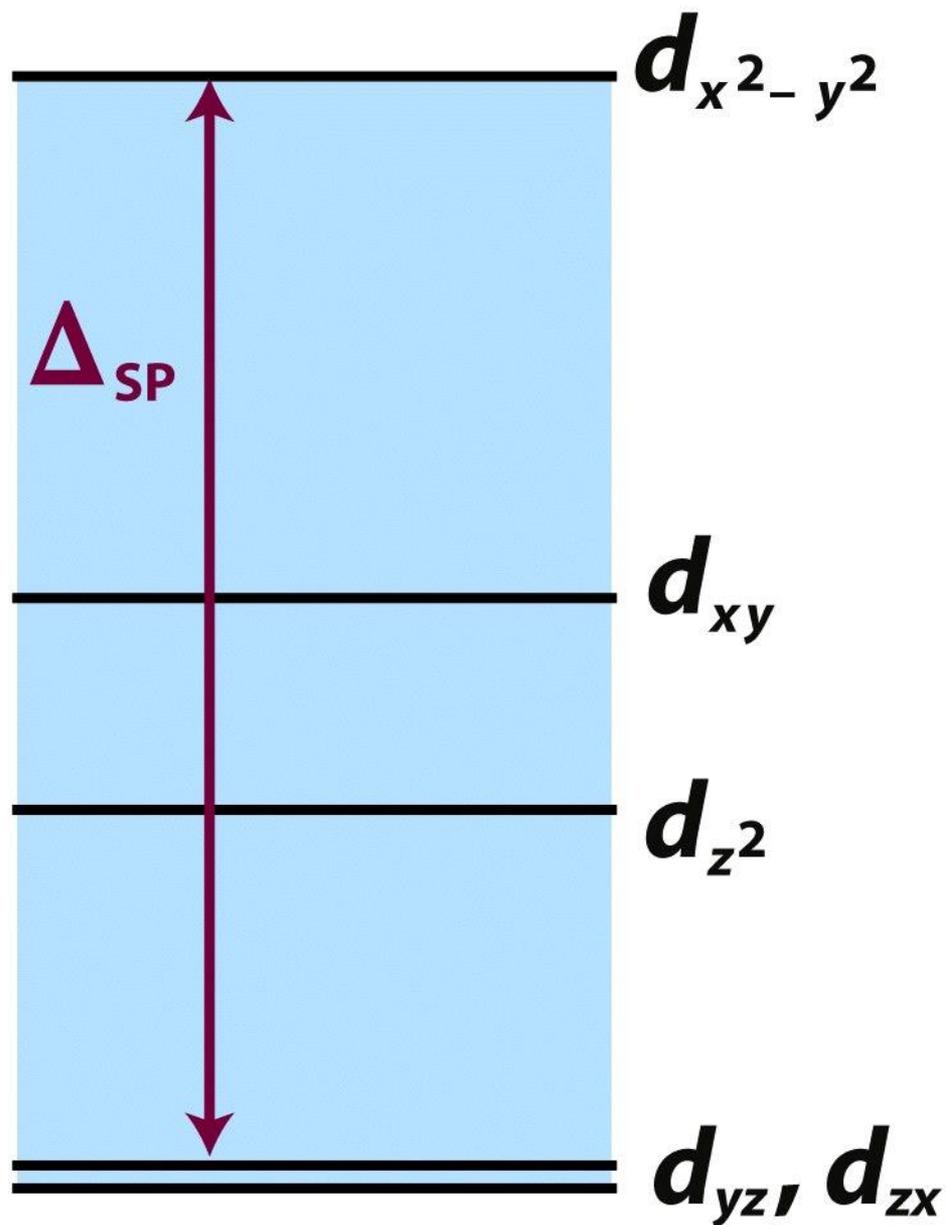




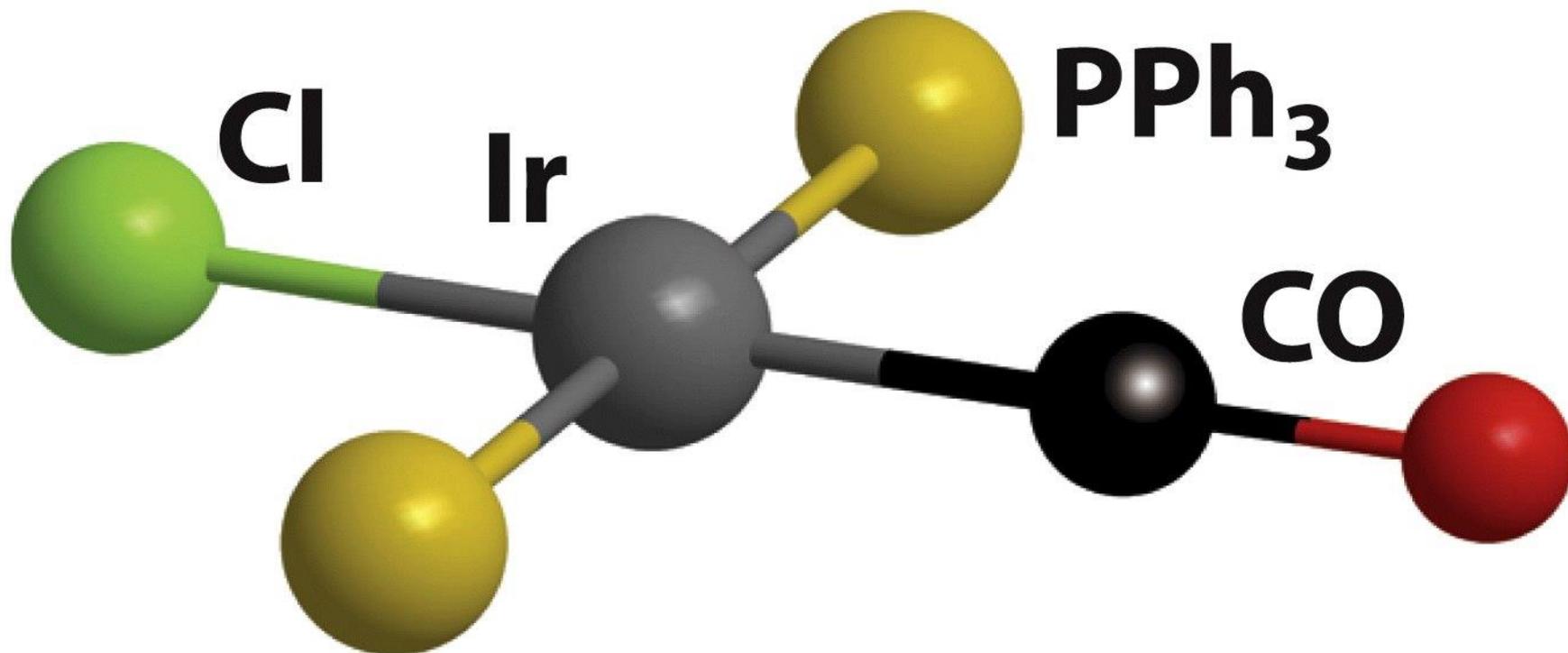




Livelli di energia per gli orbitali molecolari in un complesso ottaedrico avente leganti a campo forte (π accettori)

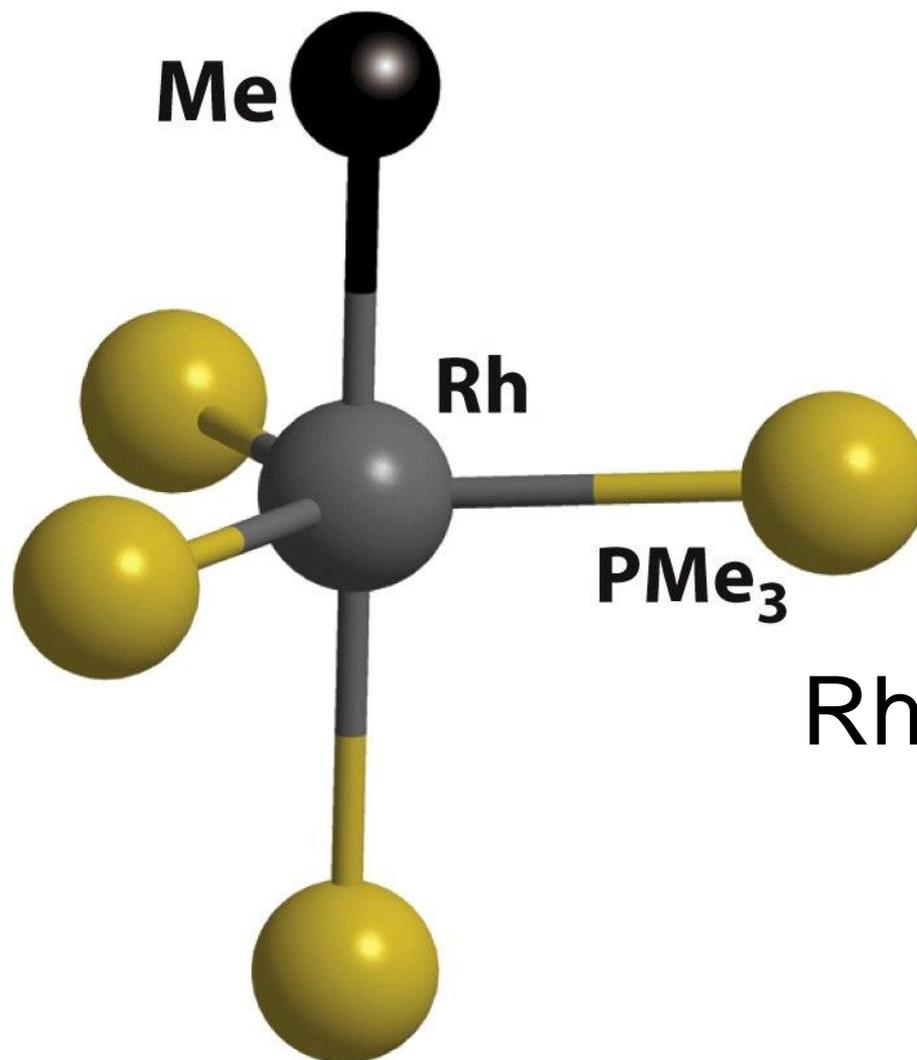


Livelli di energia degli orbitali molecolari d in un complesso planare-quadrato con leganti a campo forte.



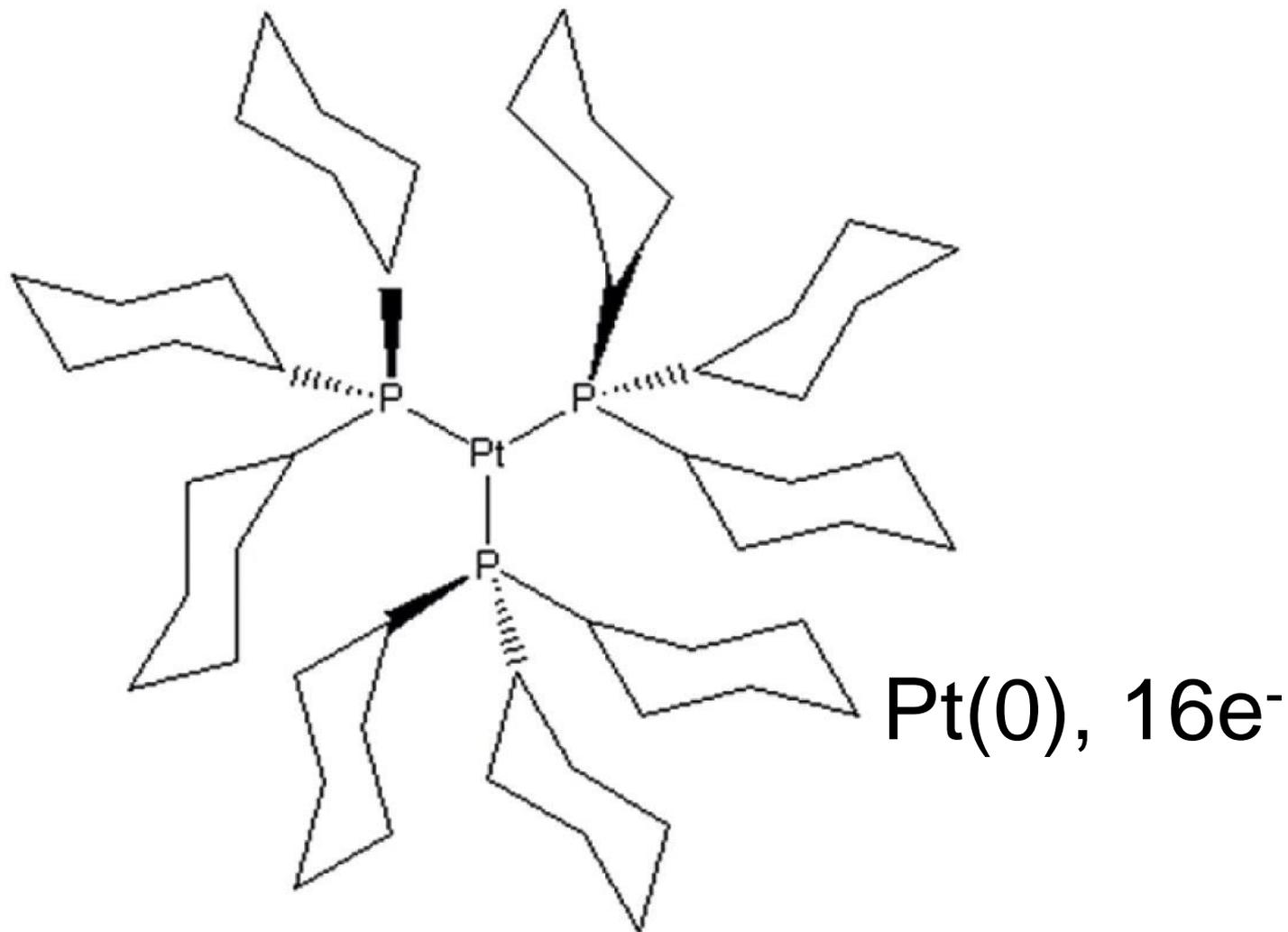
Complesso di Vaska (16e⁻)

Eccezioni alla regola dei 16-18 elettroni



Rh(I), 18e⁻

Eccezioni alla regola dei 16-18 elettroni



Eccezioni alla regola dei 16-18 elettroni

Table 21.1 Validity of the 16/18-electron rule for *d*-metal organometallic compounds

Usually less than 18 electrons			Usually 18 electrons			16 or 18 electrons	
Sc	Ti	V	Cr	Mn	Fe	Co	Ni
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
La	Hf	Ta	W	Re	Os	Ir	Pt

Eccezioni alla regola dei 18 elettroni

$[\text{V}(\text{CO})_6]$	17 elettroni
$[\text{W}(\text{CH}_3)_6]$	12 elettroni
$[\text{Cr}(\eta^5\text{-Cp})(\text{CO})_2(\text{PPh}_3)]$	17 elettroni
$[\text{Cr}(\eta^5\text{-Cp})(\text{CO})_3]_2$	18 elettroni

Cr–Cr (eptacoordinazione)

Regole di Nomenclatura

(vedi anche bibliografia su Moodle)

Nome esteso

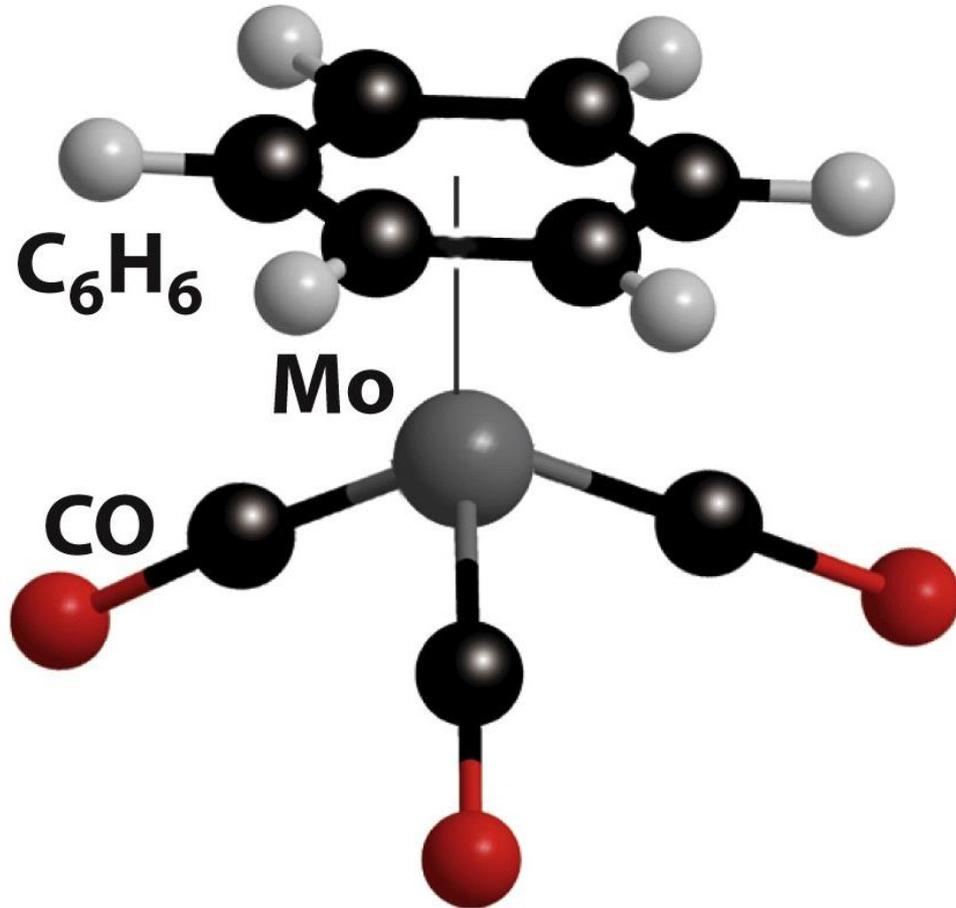
Una parola unica:

- Leganti elencati in ordine alfabetico,
- ev. con coefficienti (di, tri, tetra,... o bis, tris, tetrakis,..)
- seguiti dal nome del metallo,
- seguito dal suo numero di ossidazione in parentesi.

Formula (tra parentesi [])

- Simbolo del metallo,
- seguito dai leganti in ordine alfabetico (basato sui loro simboli chimici)

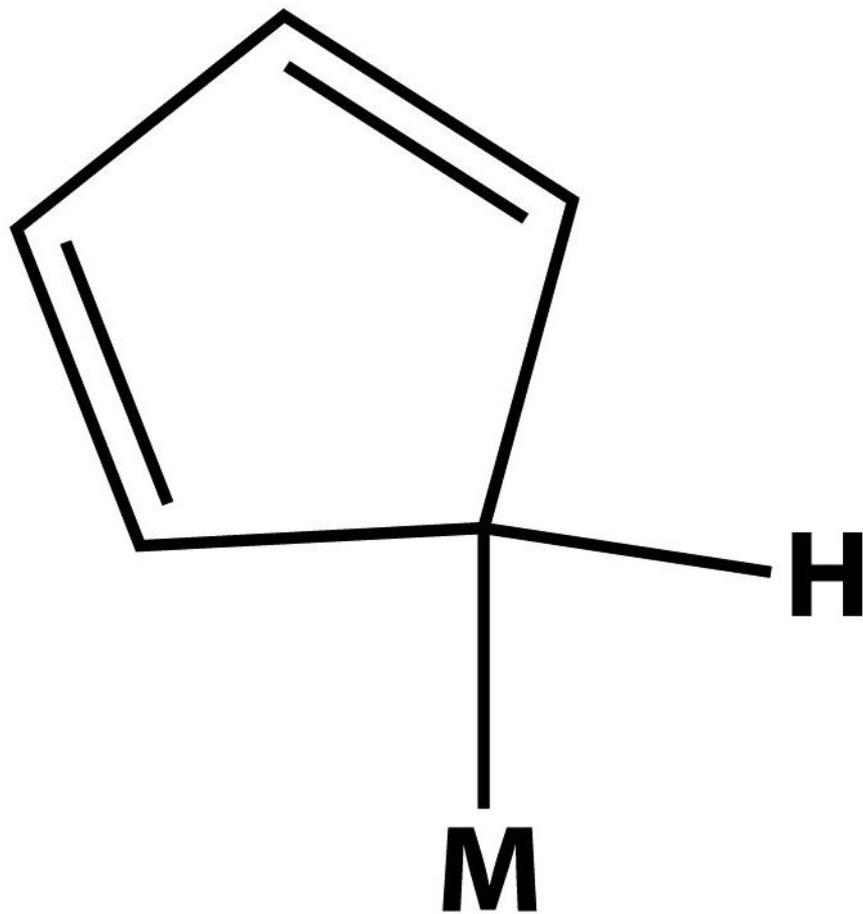
Non sempre l'ordine dei leganti è lo stesso nei due casi



benzene(tricarbonile)molibdeno(0)

benzenemolibdeno-tricarbonile

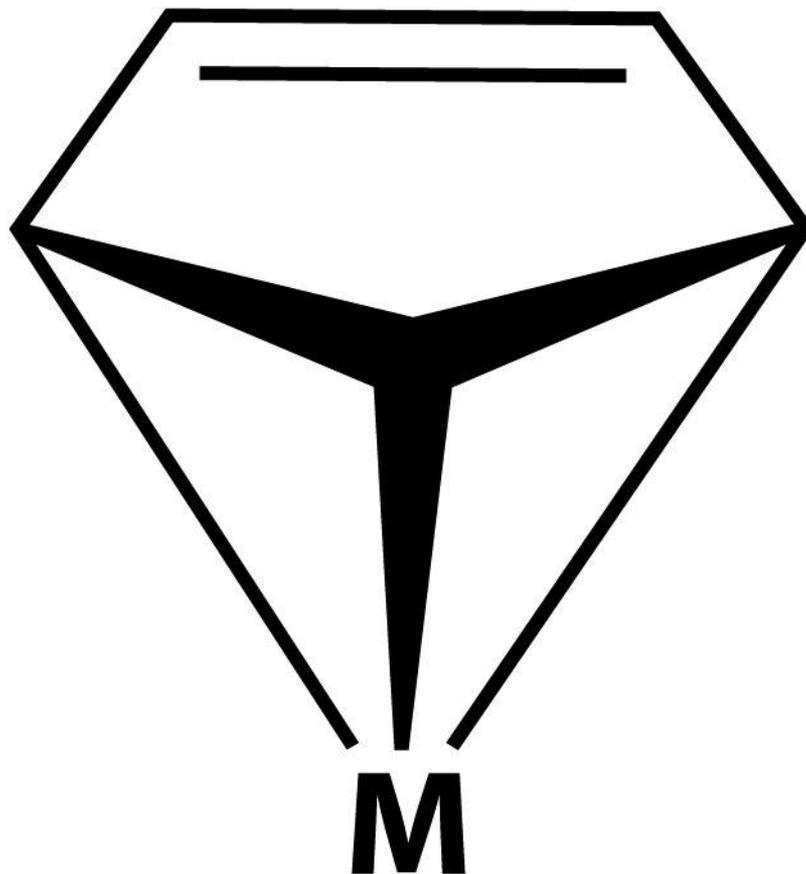




Apticità = numero di atomi del legante che - formalmente - si ritiene siano direttamente legati all'atomo metallico

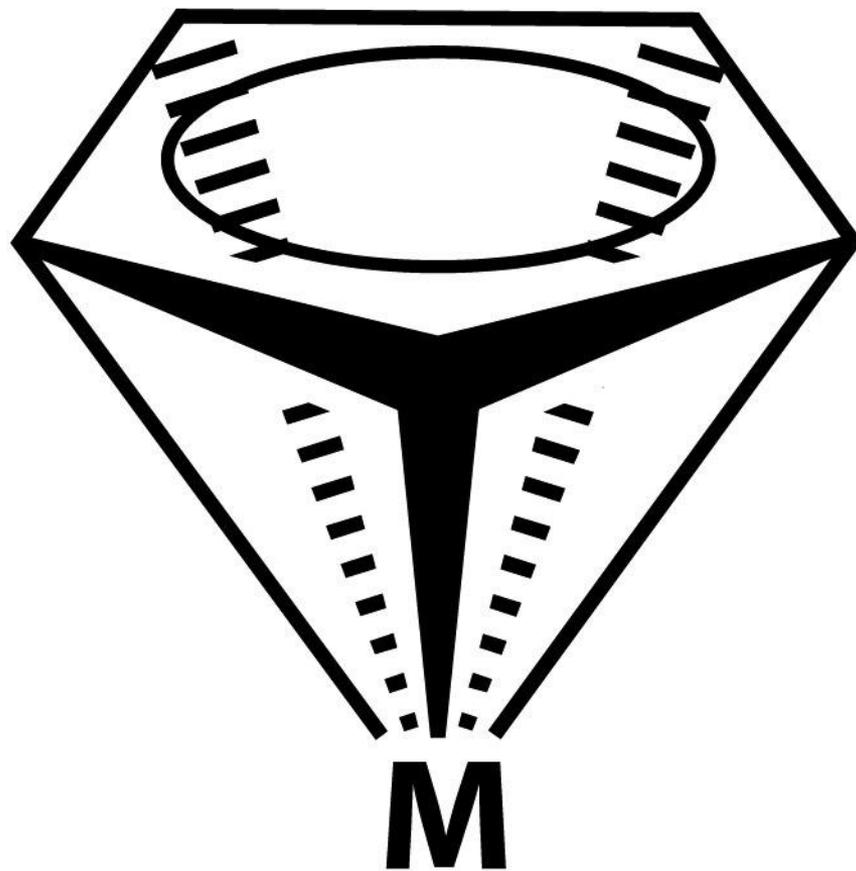
η^1 -Cyclopentadienyl

2 elettroni



η^3 -Cyclopentadienyl

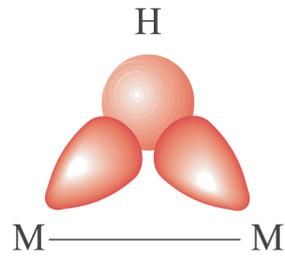
4 elettroni



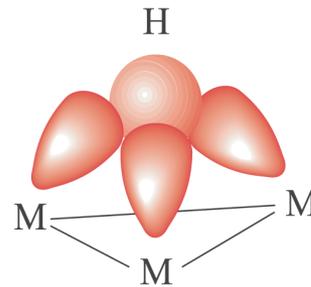
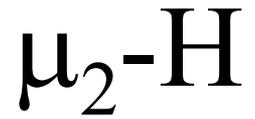
η^5 -Cyclopentadienyl

6 elettroni

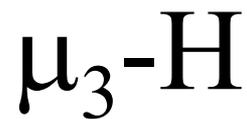
Leganti a ponte

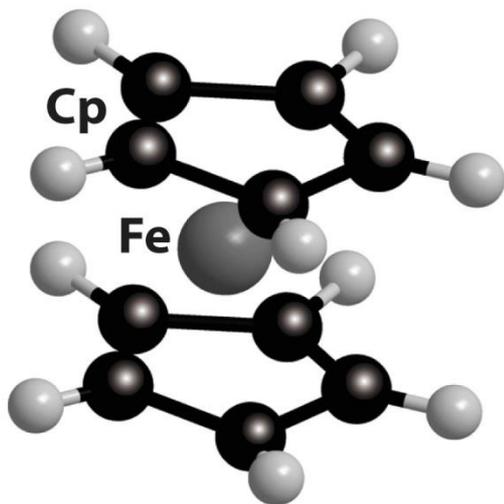


(a)

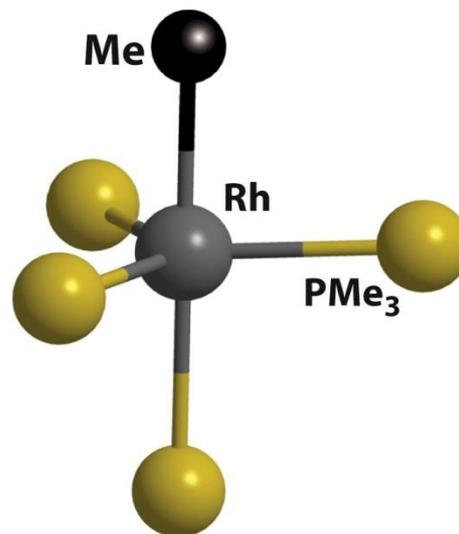


(b)

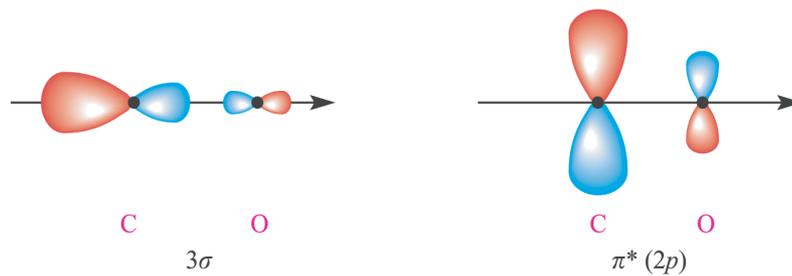
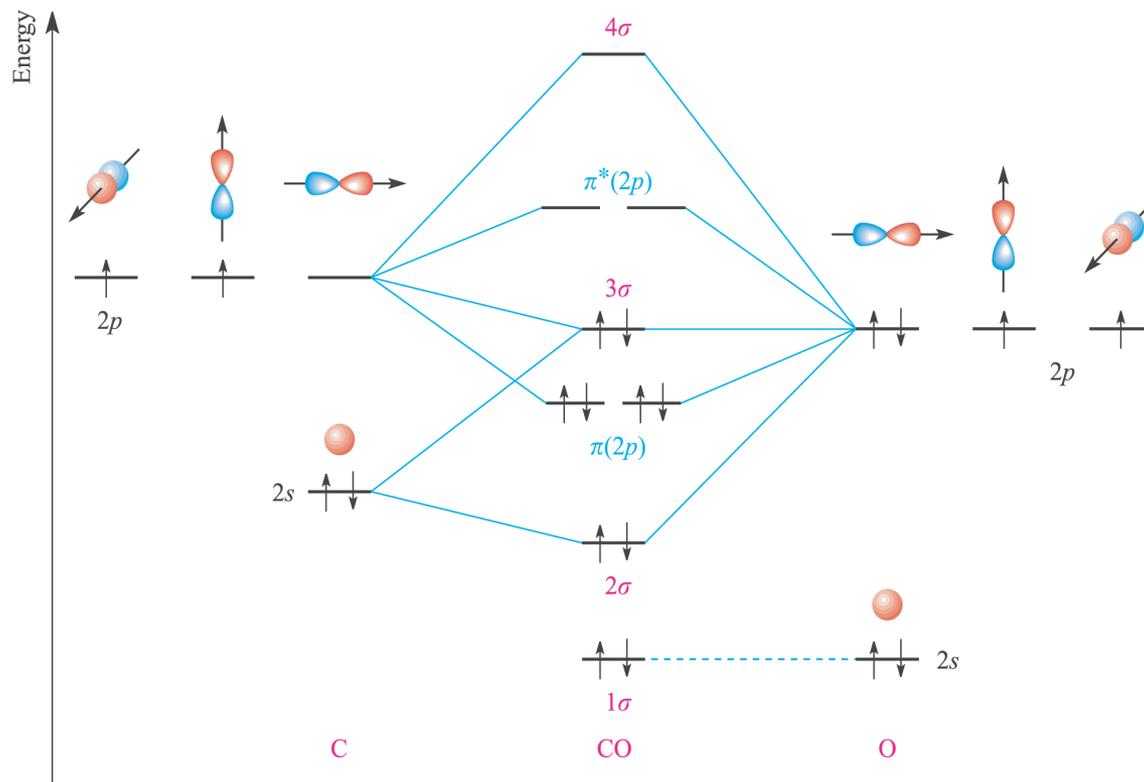




bis(η^5 -ciclopentadienil)ferro(II)

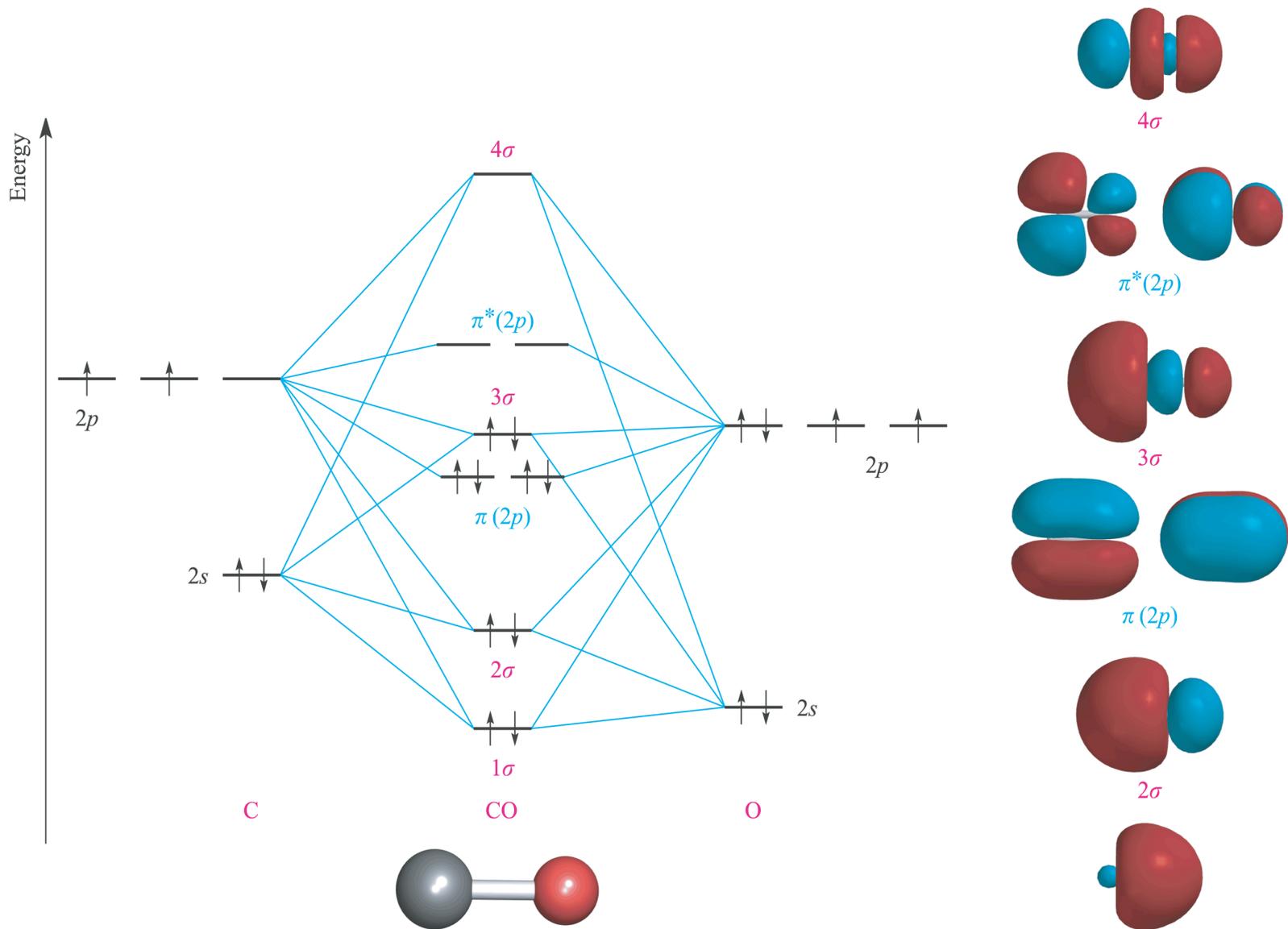


metiltetrakis(trimetilfosfina)rodio(I)

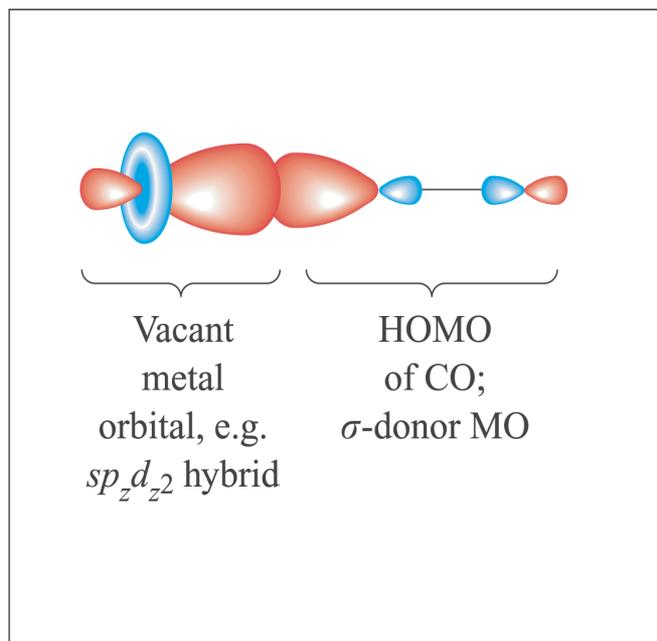
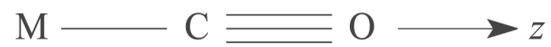


(a)

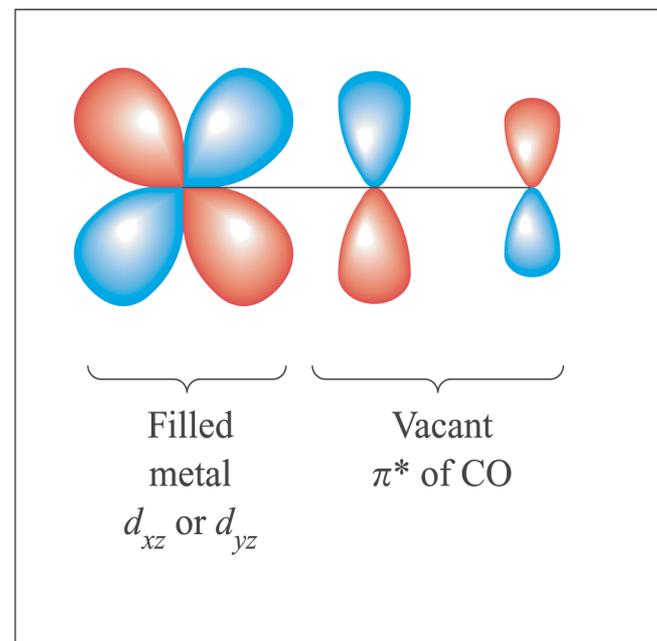
Il diagramma semplificato degli orbitali molecolari di CO



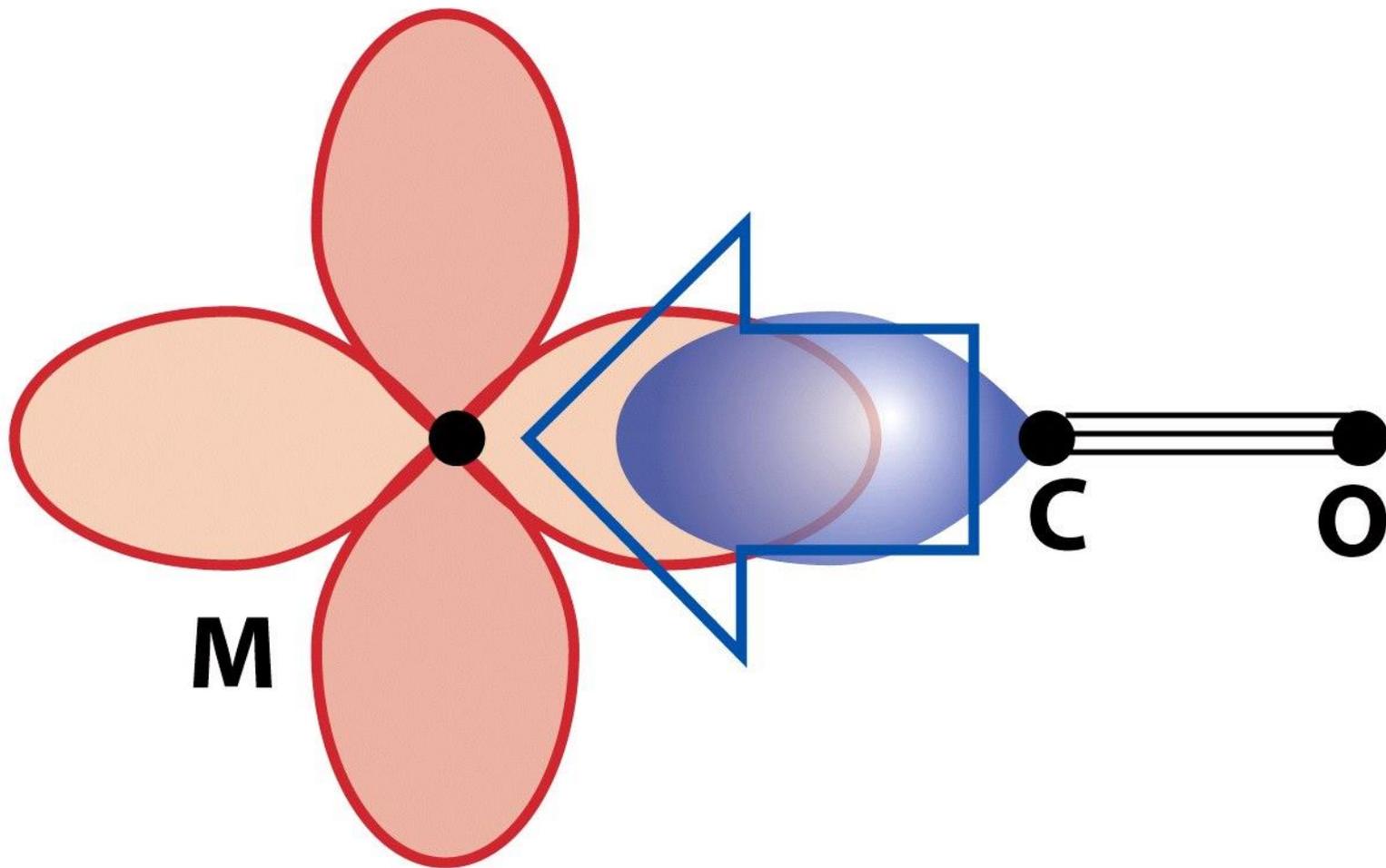
Il diagramma degli orbitali molecolari di CO mostra che l'HOMO (3σ) ha simmetria σ ed è costituito essenzialmente da un lobo su C che si proietta verso l'esterno. Il LUMO ha simmetria π .



CO-to-M donation
(a)



M-to-CO back-donation
(b)



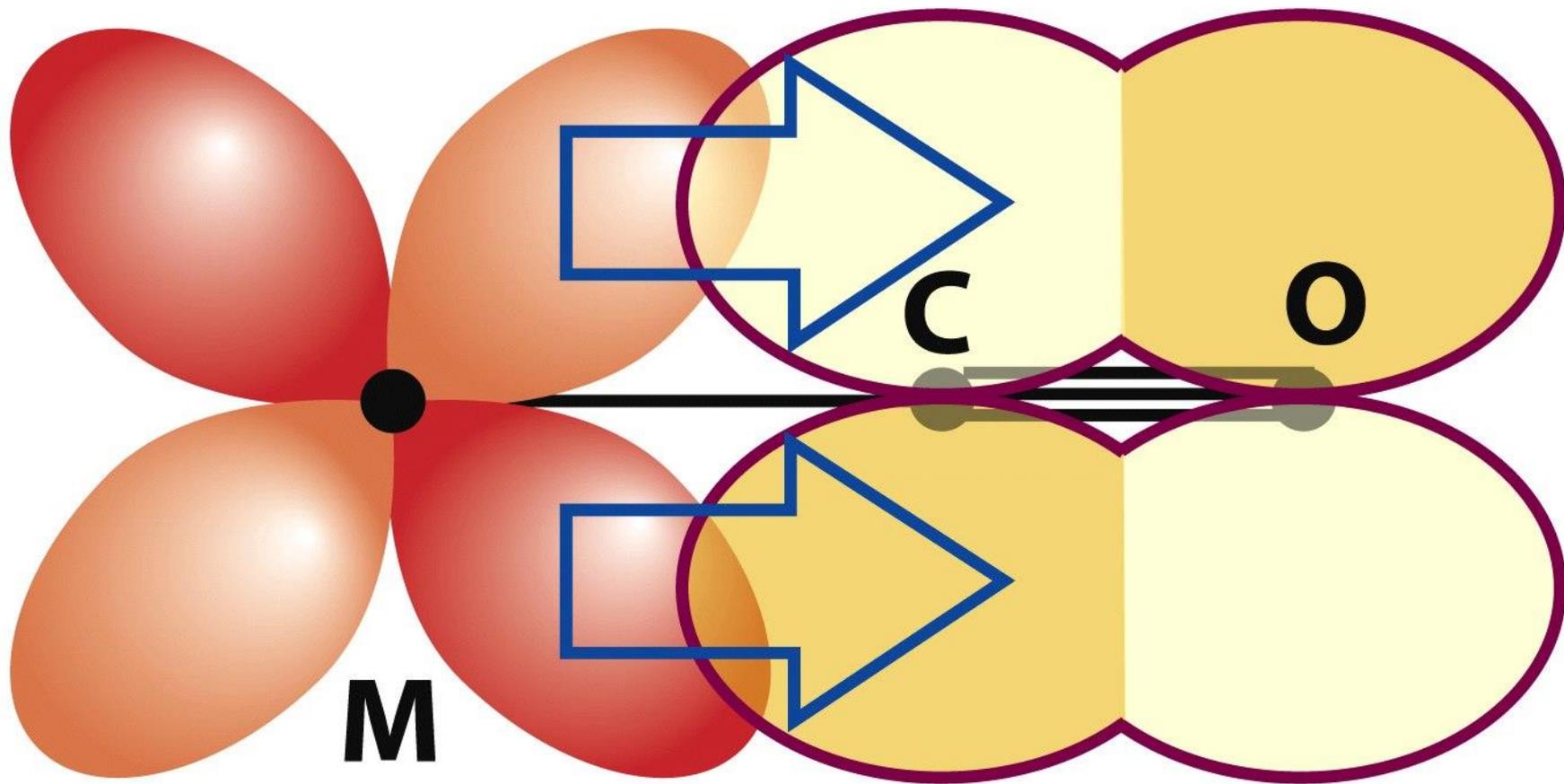
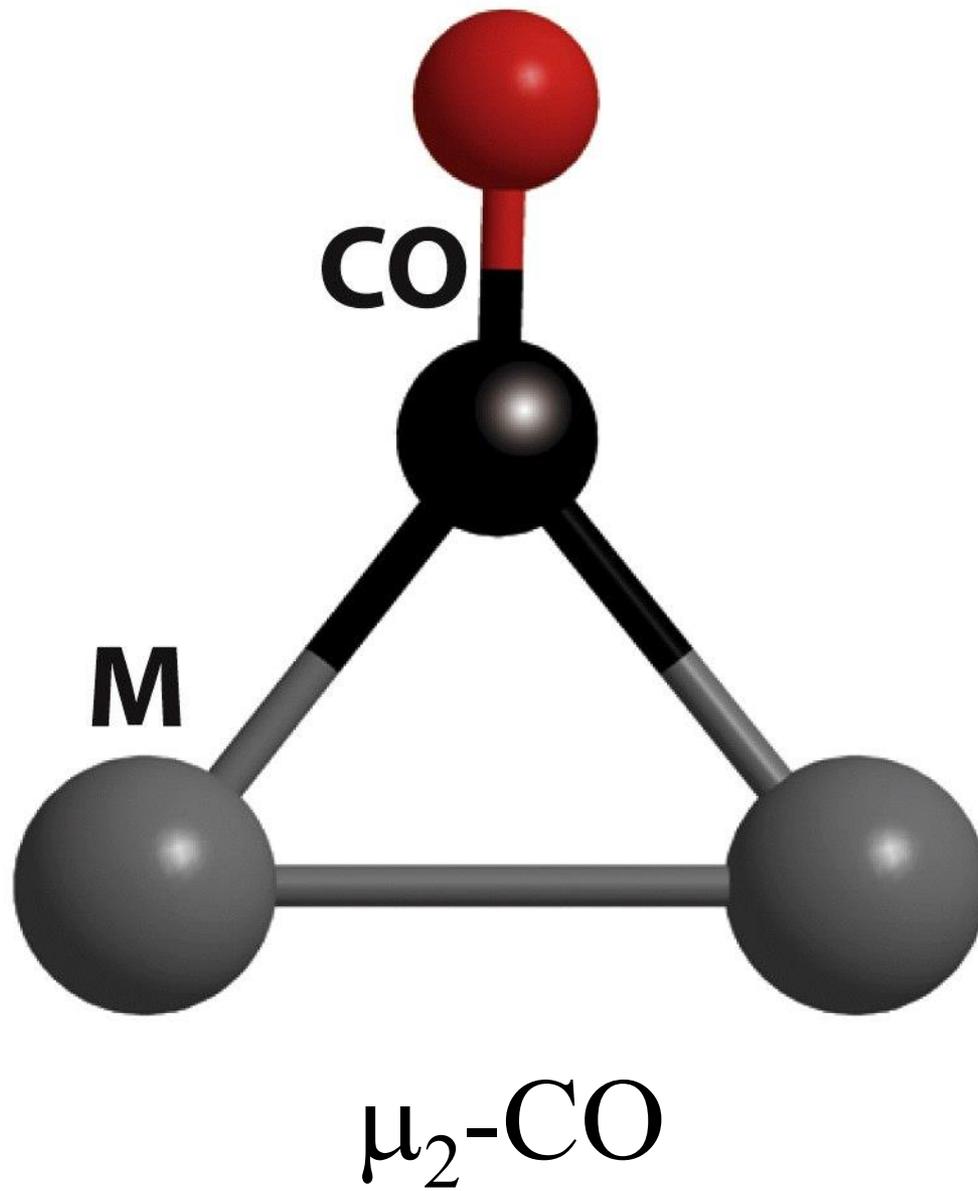
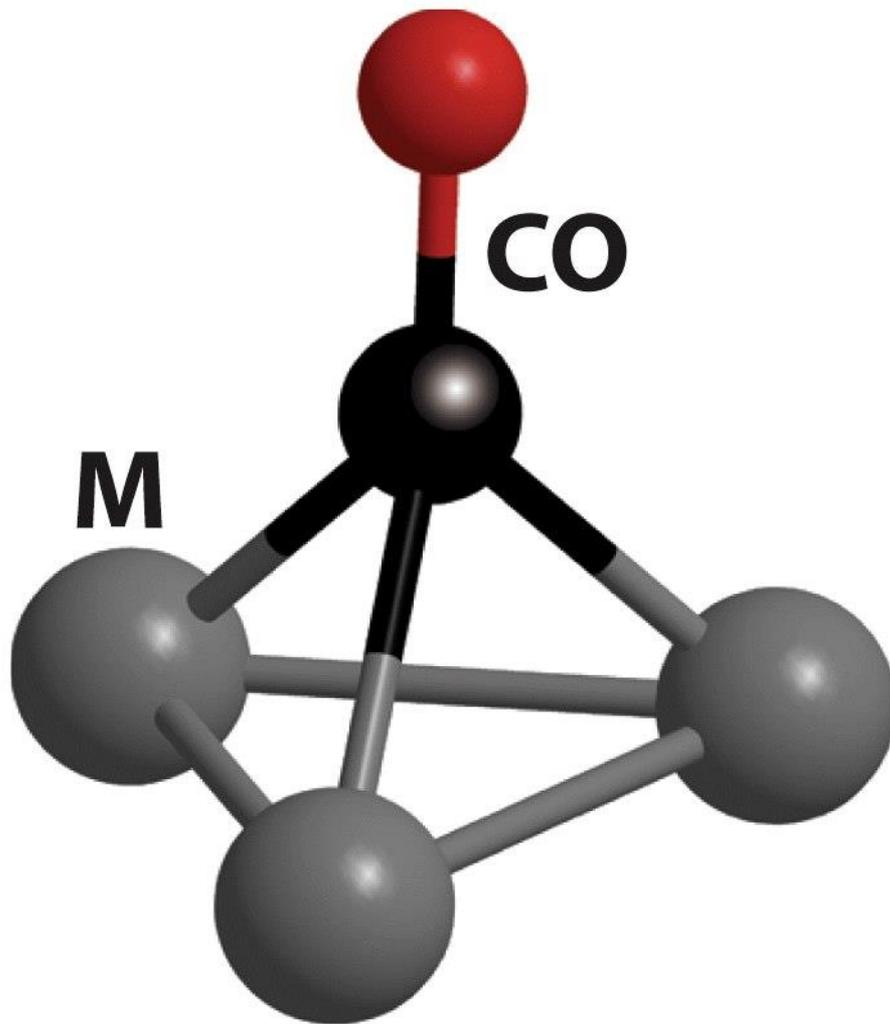


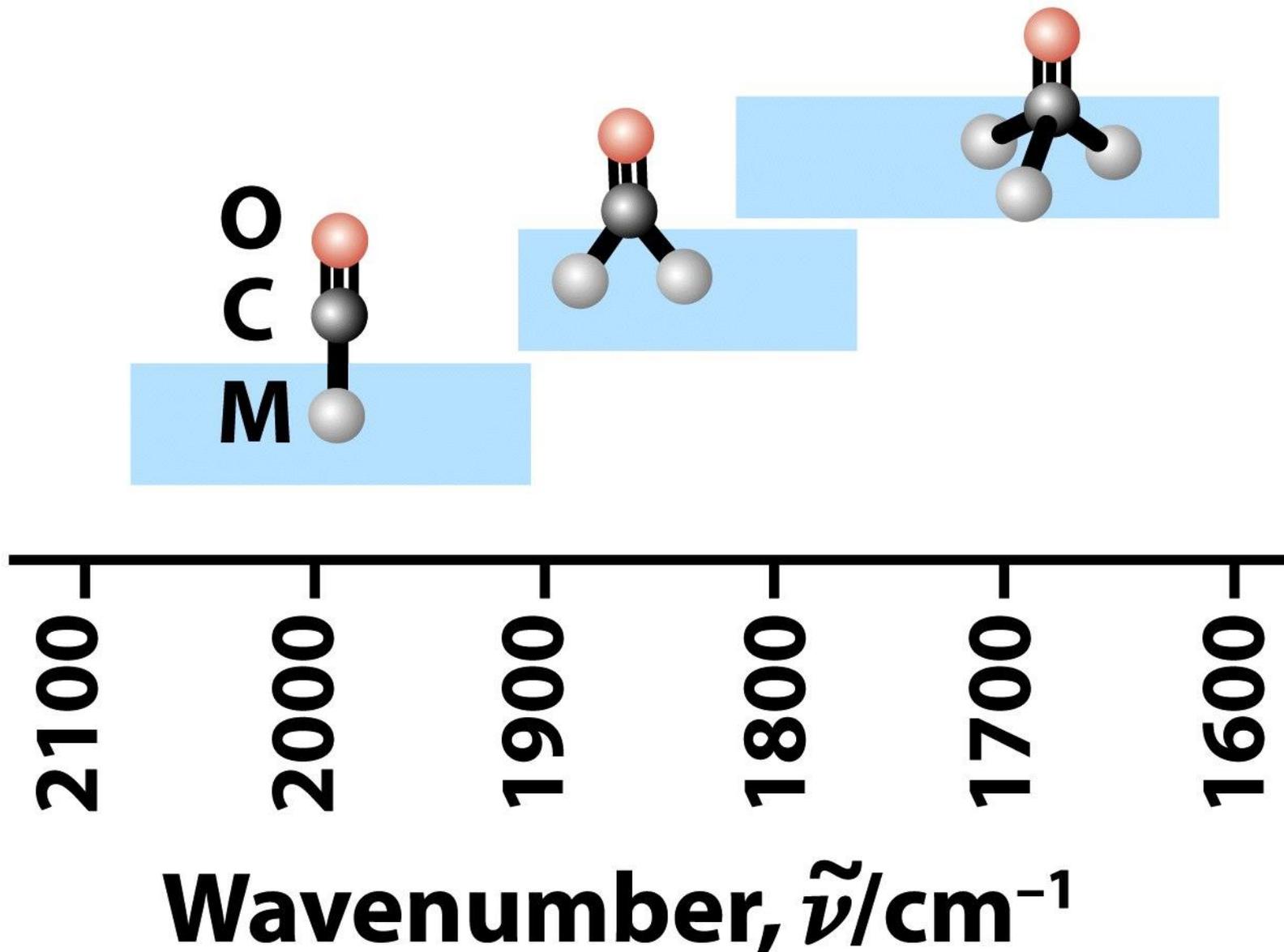
Table 21.3 The influence of coordination and charge on CO stretching wavenumbers

Compound	$\tilde{\nu}/\text{cm}^{-1}$
CO	2143
$[\text{Mn}(\text{CO})_6]^+$	2090
$\text{Cr}(\text{CO})_6$	2000
$[\text{V}(\text{CO})_6]^-$	1860
$[\text{Ti}(\text{CO})_6]^{2-}$	1750





μ_3 -CO



Intervalli approssimati per le bande di vibrazione del CO nei metallocarbonili neutri.

